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## Chapter 6

# USING MULTIPLE LINES OF EVIDENCE TO DEMONSTRATE THAT ELEVATED ARSENIC GROUNDWATER CONCENTRATIONS ARE NATURALLY OCCURRING

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**Abstract:** It has been widely documented that in many parts of New England, background concentrations of arsenic in groundwater may exceed existing and/or proposed standards. Consequently, the need to document that concentrations detected above the standard values are, in fact, representative of naturally occurring arsenic concentrations and not the result of an anthropogenic release of arsenic to the environment has become increasingly important in recent years.

The study site is located in central Massachusetts, adjacent to a tributary to a public water supply reservoir. During the course of an investigation to evaluate the potential for subsurface discharge of non-contact cooling water, groundwater samples were collected from overburden and bedrock aquifers. Laboratory analysis indicated that elevated concentrations of arsenic were present in several samples. At some of those locations, detected concentrations in overburden and bedrock groundwater exceeded the reportable concentration for arsenic under the Massachusetts Contingency Plan of 0.050 mg/l (subsequently decreased to 0.010 mg/l), which triggered the need for further evaluation of subsurface conditions.

In this study, multiple lines of evidence were used to support the position that elevated concentrations of arsenic were due to natural dissolution of arsenic-bearing minerals in the overburden and bedrock aquifers. These lines of evidence included: historical information that did not support any use or disposal of arsenic-bearing materials; available geologic mapping; field observations of overburden and bedrock encountered during well drilling; total concentrations of arsenic, iron, and manganese and microprobe analyses indicating the presence of arsenic-bearing minerals in overburden materials; and evaluation of geochemical characteristics (pH, dissolved oxygen, oxidation/reduction potential) of groundwater samples.

**Key words:** arsenic; Massachusetts; New England; Massachusetts Contingency Plan; MCP; groundwater; geochemistry; background concentration; naturally occurring arsenic.

## 1. INTRODUCTION

### 1.1 Purpose of Study

Arsenic was detected in groundwater at concentrations exceeding regulatory standards in overburden and bedrock wells at a site located within a public water supply watershed in central Massachusetts. This condition required further evaluation under applicable state regulations. Consequently, an investigation was undertaken to evaluate the source of the arsenic, specifically to determine whether or not the observed concentrations represented a naturally-occurring condition or were due to a release of hazardous materials.

## **1.2 Background Information**

Arsenic in drinking water has been widely recognized as having significant impacts on human health and has been identified as one of the leading environmental causes of cancer mortality worldwide (Welch et al., 2000). The disastrous health impacts of consumption of arsenic-contaminated groundwater in Bangladesh have been well documented and have been cited as “one of the World’s worst disasters affecting humans” (Ravenscroft et al., 2001). Worldwide, background concentrations of arsenic are typically less than 0.01 milligrams per liter (mg/l), but can range over four orders of magnitude from less than 0.0005 to 5.0 mg/l (Smedley and Kinniburgh, 2003). Over 28 million people worldwide are estimated to consume water with greater than 0.05 mg/l of arsenic, and an even larger number are exposed to concentrations greater than 0.01 mg/l (Ravenscroft et al., 2001).

In response to the mounting evidence of severe health impacts, the World Health Organization (WHO) lowered its drinking water guideline from 0.05 mg/l to 0.01 mg/l in 1993. Many international environmental authorities followed the WHO lead, including the U.S. Environmental Protection Agency (EPA), which set the Maximum Contaminant Level (MCL) at 0.01 mg/l in 2001 (Smedley and Kinniburgh, 2003).

## **1.3 Natural Arsenic Occurrence in the Environment**

Arsenic is a ubiquitous, semi-metallic element found in numerous types of environmental media, including bedrock, unconsolidated overburden materials, sediments, surface water, groundwater, and the atmosphere, as well as in the tissues of organisms. It is mobilized and redistributed in the environment through a variety of natural processes such as weathering, geochemical reactions and biological activity, and also as a result of many anthropogenic activities.

In a nationwide survey of arsenic occurrence and geochemical controls, the U.S. Geological Survey (USGS) found that concentrations of naturally occurring arsenic varied with climate and geology. Slightly less than half of 20,000 groundwater samples collected throughout the United States contained arsenic at concentrations below 0.001 mg/l, and about 10% contained arsenic at concentrations above 0.01 mg/l. The study identified New England as an area with elevated naturally occurring arsenic in groundwater that was primarily due to bedrock sulfide mineralization (Welch et al., 2000). Other USGS studies of elevated arsenic concentrations in New England drinking water, including bedrock public supply wells, attempted to correlate elevated occurrence of arsenic in groundwater with regional geology in an effort to predict where elevated concentrations may be found. These studies identified the Worcester, Massachusetts region, which includes the study area, as having arsenic concentrations in groundwater exceeding 0.02 mg/l (Ayotte et al., 2003; Ayotte et al., 2006).

Specifically, an area extending from northern Connecticut, through Massachusetts and into New Hampshire and Maine was identified as having moderate to high (0.01 to 0.05 mg/l) arsenic concentrations in groundwater-supplied drinking water. The elevated arsenic was primarily confined to bedrock water supply wells and was statistically more likely to occur in calcareous metasedimentary rock with high groundwater pH. In addition, areas of Pleistocene marine inundation and locations near granitic plutons with associated hydrothermal mineralization exhibited elevated concentrations. However, the study also reported that anthropogenic sources may also have an influence on elevated arsenic concentrations through the use of arsenical pesticides from the early 1900s through the 1960s.

## 2. REGULATORY COMPLIANCE

### 2.1 Discovery of the Arsenic Problem

The Massachusetts Water Resources Authority (MWRA) is a regional water and sewer utility that provides wholesale water and sewer service to 46 cities and 43 towns in the Boston Metropolitan area, as well as water services to several communities in the Chicopee Valley area of central Massachusetts. The source of the MWRA water supply is two large reservoirs, the Quabbin and Wachusett Reservoirs in central Massachusetts.

As part of the water transmission and distribution system, the MWRA operates a facility in West Boylston, Worcester County, Massachusetts, at the terminus of an aqueduct that connects the Quabbin and Wachusett Reservoirs. To take advantage of the head loss between these two reservoirs, a 3.5-megawatt hydroelectric generator is operated at this facility.

Arsenic was first detected in groundwater during a hydrogeological study conducted at the site in 2001 to evaluate the feasibility of recharging non-contact cooling water from the facility's hydroelectric generator directly to overburden or bedrock aquifers under a groundwater discharge permit. During the course of the hydrogeologic study, dissolved arsenic was detected in groundwater samples from the overburden and bedrock at concentrations ranging from 0.009 to 0.24 mg/l. Several samples exceeded the former Reportable Concentration for arsenic of 0.05 mg/l identified in the Massachusetts Contingency Plan (310 CMR 40.0000, the "MCP"), and the Massachusetts Department of Environmental Protection (MassDEP) was notified in accordance with MCP regulations. The MWRA was then required to investigate the nature and extent of arsenic contamination and determine if remediation was required.

### 2.2 Massachusetts Regulatory Response

Exposure to arsenic in drinking water and/or groundwater is regulated by the MassDEP under two sets of regulations. The drinking water standards are found under the Massachusetts Drinking Water Regulations, 310 CMR 22.00. In January 2006, the Massachusetts Maximum Contaminant Level (MMCL) for arsenic in drinking water was lowered from 0.05 mg/l to 0.010 mg/l, consistent with EPA requirements.

The MCP regulations pertain to releases of oil and/or hazardous materials in the environment and provide requirements for reporting, assessment, and remediation of soil and groundwater. Formal notification to MassDEP is required within a specific time-frame whenever oil or hazardous material (in this case, arsenic) is detected in soil or groundwater above MCP Reportable Concentrations. Once notification has been made to MassDEP, the property owner or responsible party is required to assess the nature and extent of the contamination. Further response actions, potentially including remediation, will be required if contaminant concentrations at the site exceed soil and groundwater cleanup standards, or if concentrations are determined to pose significant risk to human health and the environment.

Currently, the MCP cleanup standard for arsenic is 20 milligrams per kilogram (mg/kg) for all soil categories. For groundwater, the cleanup standards are 0.01 mg/l for settings where groundwater is currently or has the potential to be used as a drinking water resource and 0.9 mg/l for other groundwater uses.

For most MCP-regulated compounds, the soil and groundwater cleanup standards are risk-based and derived using highly conservative exposure assumptions. These cleanup standards are intended to be protective of the most sensitive human health receptors within the general population (i.e., infants, elderly) under unrestricted use conditions. Arsenic is an exception because "background" concentrations in soil and groundwater at many locations are higher than derived risk-based cleanup standards. The MCP defines "background" to include concentrations of contaminants that would exist in the absence of the disposal site which are, "... ubiquitous and consistently present in the environment at and in the vicinity of the disposal site of concern; and attributable to geologic or ecological conditions". Since it is not reasonable or practical to require remediation of sites to below

naturally occurring or background levels, there are provisions in the MCP to achieve a “permanent solution” or site closure if detected concentrations are consistent with background.

In April 2006, the MassDEP amendments to the MCP regulations included a notification exemption for detections of arsenic in soil and groundwater in Worcester County, provided that arsenic detected in soil or groundwater is determined to be consistent with “background” as defined in the MCP. The burden is on the property owner or responsible party to establish site-specific background conditions and demonstrate that arsenic is ubiquitous, consistently present at and in the vicinity of the site, and attributable to geologic conditions. The purpose of this paper is to provide an example of the scientific methodology used to support the position that detected concentrations of arsenic at a site in Worcester County, Massachusetts, met the requirements for designation as “background” under the MCP.

### **3. RESOLVING THE REPORTABLE CONDITION TO ACHIEVE SITE CLOSURE**

#### **3.1 Study Objectives and Approach**

The primary objective of this study was to determine whether or not the detected concentrations of arsenic in groundwater at the site could be attributed to background conditions or were due to a historical release from anthropogenic activity. Based on a general knowledge of site history and regional geology for central Massachusetts, the presence of arsenic in groundwater was suspected to be naturally occurring. To confirm this assumption, the following conditions needed to be demonstrated at the site:

1. No past or present anthropogenic sources of arsenic at the site.
2. Soil and/or bedrock at the site contain arsenic-bearing minerals or weathering products.
3. Geochemical parameters in the aquifer are favorable for dissolution of arsenic-bearing minerals and mobilization of arsenic into groundwater.

Each condition by itself would not be adequate to support the assumption that arsenic is naturally occurring. Combined, however, these “lines of evidence” could provide the necessary justification that arsenic concentrations detected in groundwater at the site are the result of naturally occurring, background conditions. For this study, each line of evidence was evaluated, and the findings are discussed below.

### **4. FIRST LINE OF EVIDENCE: ON-SITE ANTHROPOGENIC SOURCES OF ARSENIC**

#### **4.1 Site Description and History**

The site consists of approximately five acres of undeveloped, wooded public water supply watershed land located along the southern bank of the Quinapoxet River. As shown in Figure 1, two granite and masonry buildings exist on the site. The building designated “Wachusett Outlet Building” contains the hydroelectric turbine and generator and was built in 1929-1931. The Service Building was constructed during the late-1930s and is currently used for equipment storage. The hydroelectric generating equipment was added to the outlet building in the 1940s.

Historically, the site was part of Oakdale Village, a mill community established sometime between 1815 and 1850. The first mill was built in 1814 for the manufacture of wire fabric and cotton cloth. A sawmill, which was later expanded to include cotton spinning machinery, was built during the

1820s along the Quinapoxet River east of and adjacent to the present-day site. The mills were destroyed by fire in 1853 and later replaced by a larger stone mill complex (Whitcomb, 2002).

Most of Oakdale Village was abandoned and demolished prior to 1897, when construction of the Wachusett Dam and Reservoir began. It is theorized that around that time, a low-permeability subsurface berm was constructed at the site parallel to the riverbank to prevent meandering of the river. The origin of the berm material is unknown but is assumed to be from local sources. This berm is apparent as a topographic ridge in the northwestern margin of the site on Figure 1.

Construction of the MWRA tunnel terminal shaft began in 1926. Based on review of historic photographs, it is believed that at least some of the material used for re-grading portions of the site consisted of rock spoils from tunnel construction activities. Archived construction photographs document that at least some of the soil used for regrading came from off-site locations. There have been no significant on-site changes since construction of the Service Building in the late-1930s and installation of the hydroelectric generating equipment in the 1940s.

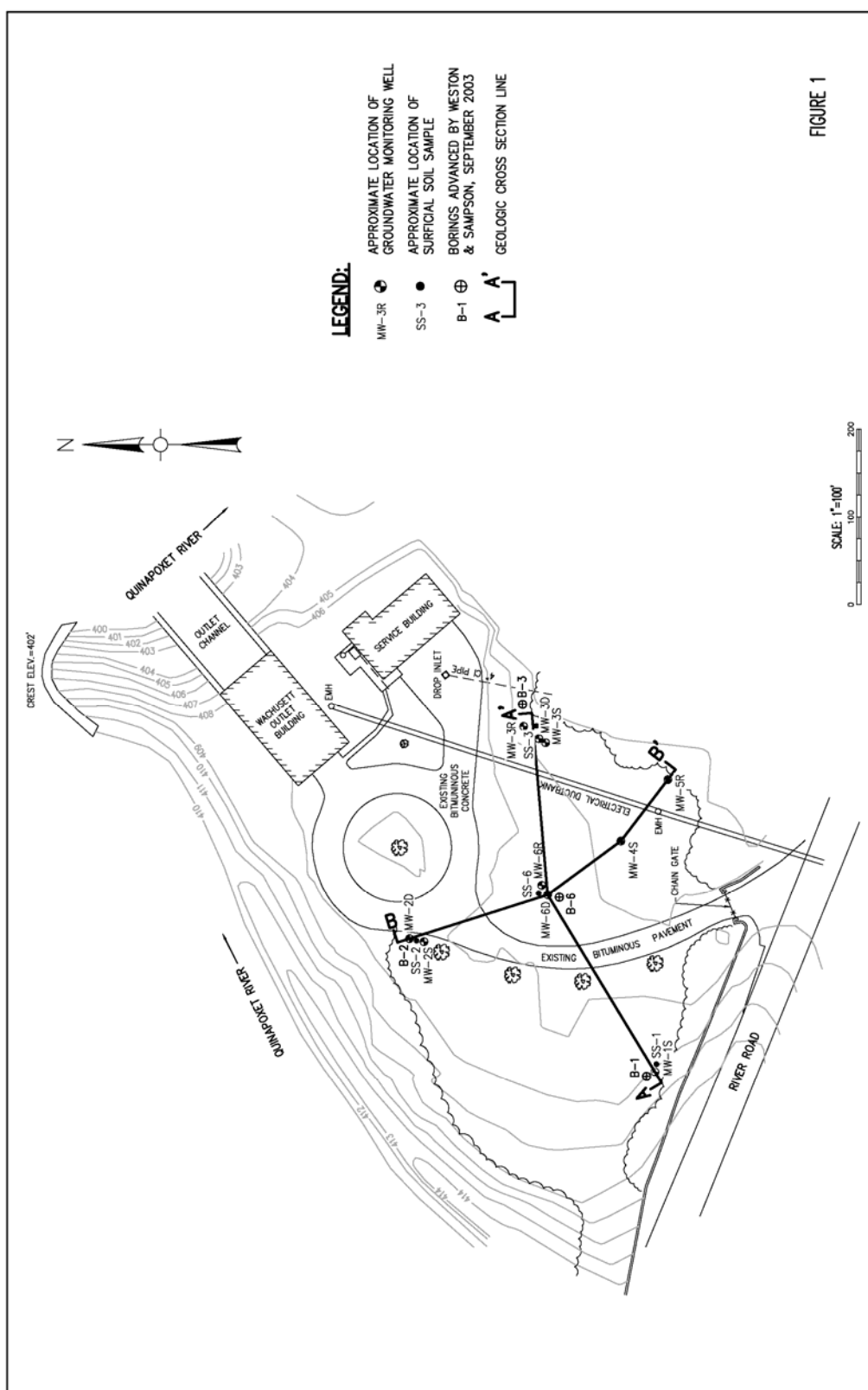


Figure 1. Site Plan

## **4.2 Potential Anthropogenic Sources of Arsenic**

Many anthropogenic activities have contributed to arsenic in the environment including combustion of fossil fuels, mining and smelting operations, manufacture and application of pesticides and herbicides, and as an additive to livestock feed (Smedley and Kinniburgh, 2003). Primary industrial uses of arsenic include metallurgy for hardening of copper, lead and alloys, and in the manufacture of glass, insecticides, and wood preservatives (Agency for Toxic Substances and Disease Registry, 2001). In the U.S., the major anthropogenic sources of arsenic in soil over the past century have been attributed to wood preservatives and pesticide applications. Chromated copper arsenate (CCA) has been used since the 1930s to prevent rotting of wood. CCA-treated wood is used predominantly on outdoor decks and structures, and accounts for over 90% of arsenic used today in this country (Welch et al., 2001). CCA-treated wood is not considered a potential source of arsenic at the site because no wooden structures are present.

The other significant man-made source of arsenic is the historical use of pesticides. Lead arsenate, which was first prepared and used in Massachusetts in 1892, was the most widely used pesticide in the country until DDT was manufactured for commercial use in the late 1940s. Its use in New England apple orchards during the first half of the century is well documented (Peryea, 1998; Welch et al., 2000). Although there is no knowledge or records of pesticide use at the site, it cannot be ruled out as a potential source in surficial or shallow soil. According to various studies, however, arsenic released into the environment from pesticide application is relatively immobile and concentrates in the upper 25 centimeters (cm) (0.8 feet) of soil (Peryea, 1998).

As noted above in Section 2.1, arsenic was detected in several monitoring wells at the site. In addition, as is discussed in more detail below in Section 6.2, the highest arsenic concentrations were found in monitoring wells screened in deeper portions of the overburden aquifer, most notably monitoring wells MW-2D and MW-6D (depicted on Figure 1). The presence of arsenic in groundwater from well MW-2D (screened from 16 to 31 feet below grade) or from well MW-6D (screened from 40 to 64 feet below grade), is, therefore, unlikely to be associated with former pesticide application.

In summary, there have been no known anthropogenic sources of arsenic that would account for its presence in groundwater at the site. Former mill industries near the site were not known to have used and/or manufactured arsenic compounds. Arsenic is also not associated with operation of the hydroelectric power station or with waterworks operations, which have been the primary use of the facility for more than 60 and 80 years, respectively. Even if pesticides containing arsenic were used in the past, there would have been little to no impact on groundwater at depths up to 64 feet below grade due to its limited mobility in soil. Based on these findings, the first line of evidence for this study (no on-site anthropogenic sources) was confirmed.

## **5. SECOND LINE OF EVIDENCE: REGIONAL AND SITE GEOLOGIC CONDITIONS**

### **5.1 General Considerations**

The presence of elevated arsenic in groundwater due to weathering of bedrock and overburden containing arsenic-bearing minerals is well documented in various regions of the country, including central Massachusetts (Walsh, 2002; Hon et al., 2002). The second line of evidence to be evaluated at the site was to determine if the soil and/or bedrock geology contained arsenic-bearing minerals, thereby providing a potential source of arsenic to groundwater.

The subsurface geology described below is based on published regional data and sampling results obtained specifically to evaluate the occurrence of arsenic in groundwater at the subject site. For this investigation, soil samples were collected and analyzed for arsenic, related metals, and various geochemical parameters. Bedrock samples were not collected or analyzed, since the bedrock wells had already been installed prior to initiation of the arsenic investigation and because the focus of the



prior study was on hydrogeologic aquifer characteristics, rather than chemical properties. However, significant data exist on the chemical composition of bedrock in the region, and the natural overburden materials at the site, which are of glacial origin, are likely derived from regional bedrock.

## 5.2 Bedrock Geology

### 5.2.1 Regional Bedrock Geology

The USGS bedrock geology map for the Nashua River drainage basin identifies bedrock underlying the site and surrounding region as igneous and metasedimentary from the Paleozoic and Precambrian eras. Edward Grew, a doctoral candidate from Harvard University, mapped the bedrock in the vicinity of the site as the Oakdale Formation, a geographically widespread heterogeneous grouping of metasiltstone with phyllite, calcareous quartzite, calcareous siltstone, and minor schist. He described the Oakdale Formation in this area as “fine grained, purple-gray to gray biotite schist and granulite and green-gray to gray calc-silicate granulite” (a.k.a. quartzite). Trace amounts of pyrite were observed in some of the thin sections prepared from hand samples collected from this area of the Oakdale Formation. The Oakdale formation locally contains beds of carbonaceous or sulfidic mica schist or phyllite. Arsenic is often seen in sulfide minerals, typically substituting for iron (for instance, in minerals such as pyrite), and as arsenopyrite (Grew, 1970).

In 1992 the MWRA geologist David Ashenden produced a comprehensive geological report of the Wachusett Reservoir area. In his report, Ashenden retained the “Oakdale Formation” terminology used by Grew for the rocks in the Oakdale area, rather than the Littleton Formation, which is used in the Bedrock Geological Map of Massachusetts (Zen, 1983). Ashenden considered the rock exposed in the Quinapoxet River adjacent to the site and on a nearby hillside as the type location for the subdivision of the Oakdale that he called “Oakdale west of the Wekepeke Fault,” a regional fault located approximately 1,500 feet east of the site. He described these rocks as “gray, thinly laminated to poorly foliated, fine-grained, biotite quartzite”. Ashenden examined the hand samples collected from beneath the site during shaft and tunnel construction, and most significantly, found that some of the samples had small sulfide mineral grains (Ashenden, 1992).

### 5.2.2 Site-Specific Bedrock Geology

During the initial hydrogeological study described in Section 2.1, three bedrock wells (MW-3R, MW-5R and MW-6R) were drilled to depths ranging from 220 to 245 feet below grade. The depth to bedrock at these locations ranged from 45 to 65 feet below grade.

The bedrock was highly weathered in the top 8 feet. Fracture zones were observed in all bedrock borings, the most numerous of which were found in the borehole for well MW-6R at multiple depths below grade (≈80-105 feet, ≈116-119 feet, ≈131-133 feet and ≈155 feet). The rock was described as a fine-grained, alternating reddish-brown and dark green quartz mica phyllite with quartz veins. Using the formation terminology from The Bedrock Geological Map of Massachusetts, the bedrock was ultimately identified as being representative of the Littleton Formation based on ease of drilling and mineralogy of the bedrock cuttings from the borehole. The Littleton Formation consists of interbedded gray to dark-gray biotite-muscovite-quartz schist and gray quartzite (Zen, 1983).

As noted above, hand samples collected from beneath the site were found to contain small sulfide mineral grains (Ashenden, 1992). Therefore, based on observations of bedrock from the site and regional geologic information, it is reasonable to conclude that bedrock beneath the site contains arsenic-bearing minerals.

## 5.3 Overburden Geology

### 5.3.1 Regional Overburden Geology

Geological mapping of the Quinapoxet Valley during the design of the Quabbin Aqueduct in the late 1920s interpreted the surficial deposits in the eastern end of the aqueduct to be modified glacial drift including morainal, glacial lake deposits, and outwash sands and gravels. In the immediate vicinity of the site, these were more specifically identified as glacial moraine deposits (Ashenden, 1992).

The amount of published regional data for overburden is more limited than that found for bedrock. In a soil study conducted by Hon et al. (2002) elevated concentrations of arsenic (20 to 800 mg/kg) were found in sections of overburden within a zone transversing N-S across central Massachusetts.

### 5.3.2 Site-Specific Overburden Geology

Seven monitoring wells screened in the overburden aquifer were installed during the hydrogeological investigation (locations are shown on Figure 1). Table 1 summarizes the construction details of overburden and bedrock monitoring wells.

*Table 1. Monitoring well construction details*

<b>Well ID</b>	<b>Screened Interval (feet below ground surface)</b>	<b>General Lithology in Screened Interval</b>
MW-1S	5 – 20	Sand/Gravel and Silt/Clay Combination
MW-2S	4.5 – 19.5	Sand/Gravel and Silt/Clay Combination
MW-2D	16.5 – 31.5	Silt/Clay
MW-3S	4.5 – 19.5	Sand/Gravel
MW-3D	24.5 – 34.5	Sand/Gravel and Silt/Clay Combination
MW-3R	55 – 255 <sup>a</sup>	Bedrock
MW-4S	5 – 20	Sand/Gravel
MW-5R	75 – 275 <sup>a</sup>	Bedrock
MW-6D	40 – 64	Silt/Clay
MW-6R	71.5 – 275 <sup>a</sup>	Bedrock

<sup>a</sup> The indicated screened interval for the bedrock wells represents the open-hole interval.

Generalized geologic cross-sections are shown in Figure 2. The uppermost unit across most of the site appears to be an artificial fill material that is likely associated with re-grading of the site during various phases of its development. This fill material generally consists of fine- to medium-grained sand with some pebbles and cobbles. Native unconsolidated materials consisting of sand/gravel deposits ranging in thickness from approximately 10 to 35 feet were observed underlying the fill unit across the site, increasing in thickness from west to east, as shown in cross-section A-A'. As shown in cross-section B-B' (north-south), the sand/gravel unit is thickest at location MW-6D/6R.

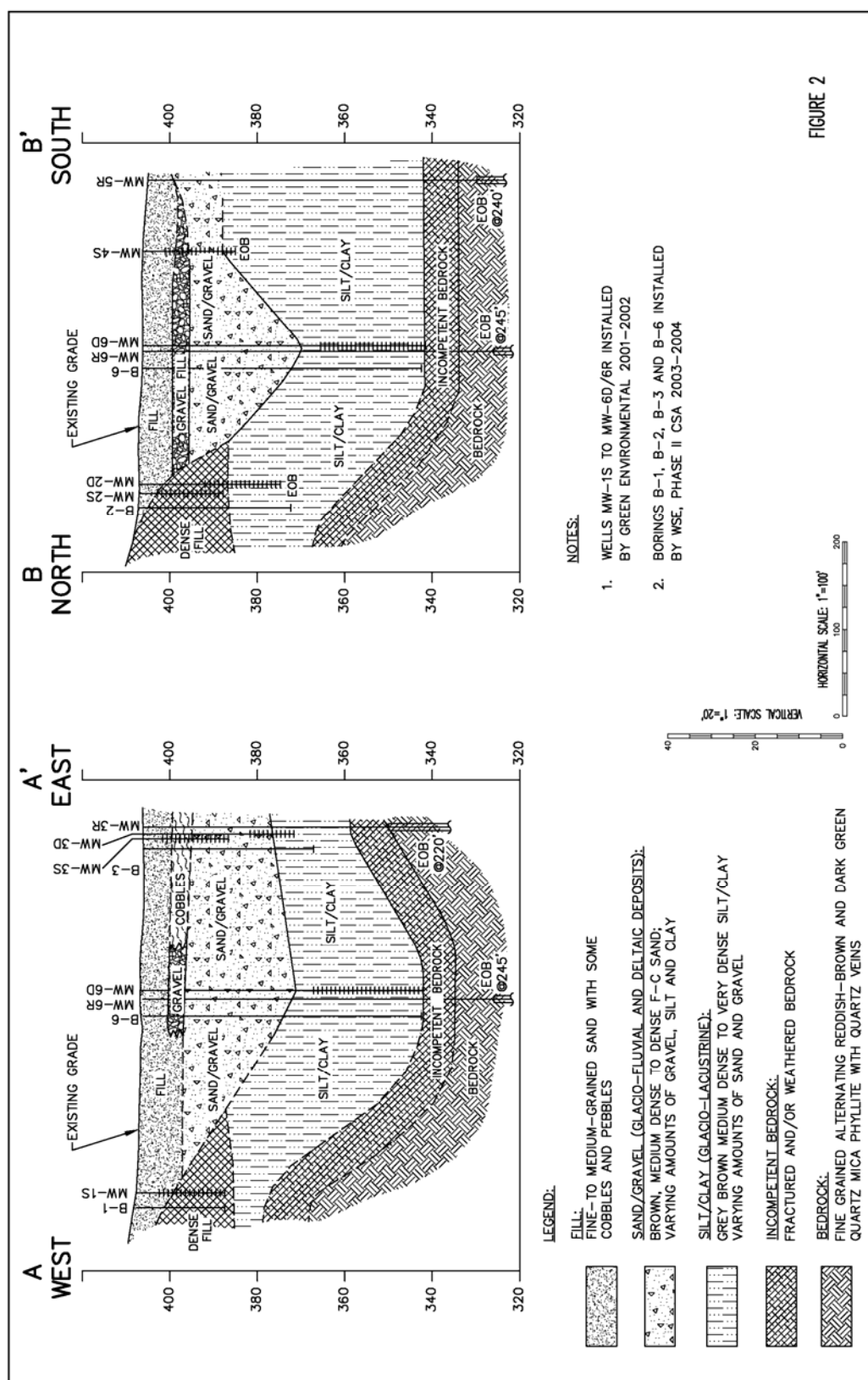


Figure 2. Geological Cross Sections: A-A' and B-B'

The native deposits consist of dense silty sand in the vicinity of well MW-1S and sand and gravel of presumably glaciofluvial/glaciolacustrine origin on the eastern portion of the site in the vicinity of groundwater monitoring wells MW-4S and MW-3S. This distribution is consistent with the regional topography and with information provided on the surficial geologic map, which indicates the presence of glacially derived sand and gravel in the vicinity of stream valleys in the region. The silt/clay layer underlying the sand/gravel unit ranges in thickness from approximately 20 to 50 feet. The dense silt encountered in the vicinity of the MW-2 well cluster appeared “non-native” and was likely placed as part of dam construction to prevent future lateral meandering of the Quinapoxet River.

## 5.4 Arsenic Concentrations in Overburden

A total of 35 soil samples from four borings were collected during drilling at the study site and submitted for laboratory analyses for arsenic, iron, and manganese. Table 2 summarizes the results of the laboratory analysis and includes the generalized stratigraphic interval from which each sample was collected. The cross-sections in Figure 2 contain more detailed descriptions of the stratigraphy comprising each generalized stratigraphic interval.

Most of the soil samples (29 of 36) contained arsenic at concentrations less than the MCP cleanup standard and “background” concentration of 20 mg/kg. The highest arsenic concentration (115 mg/kg) was detected at 8 to 10 feet in boring MW-1S. Most of the samples in this boring up to a depth of 16 feet below grade contained concentrations above 20 mg/kg. The concentrations in all other borings were below 20 mg/kg, except for samples collected from 0 to 3 feet in boring MW-2D, which ranged from 27 to 32 mg/kg. In general, the laboratory data also indicated that higher arsenic concentrations were found in samples that also contained higher iron and manganese concentrations, which would not occur if arsenic were attributed to anthropogenic sources.

Table 2. Soil analytical results

Boring	Sample Depth (ft.)	Arsenic (mg/kg)	Iron (mg/kg)	Mn <sup>a</sup> (mg/kg)	Stratigraphic Interval
MW-1S	0 – 1	23	---	---	Sand/Gravel
	0 – 3	47	16	21	Sand/Gravel
	6 – 8	16	26	40	Sand/Gravel
	<b>8 – 10</b>	115	49	41	Sand/Gravel
	<b>10 – 12</b>	27	18	24	Silt/Clay
	12 – 14	16	18	18	Silt/Clay
	14 – 16	22	20	20	Silt/Clay
	<b>18 – 20</b>	7	18	20	Silt/Clay
	20 – 22	11	---	---	Silt/Clay
	DUP	8	23	31	Silt/Clay
	<i>Mean</i>	<i>29</i>	<i>23</i>	<i>27</i>	
MW-2D	0 – 1	27	---	---	Sand/Gravel
	0 – 3	32	19	26	Sand/Gravel
	<b>17 – 19</b>	17	18	25	Silt/Clay
	19 – 21	14	18	24	Silt/Clay
	21 – 23	10	17	22	Silt/Clay
	23 – 25	5	11	15	Silt/Clay
	25 – 27	7	14	16	Silt/Clay
	<b>27 – 29</b>	6	13	15	Silt/Clay
	29 – 31	7	18	19	Silt/Clay
	31 – 33	7	16	16	Silt/Clay
	<i>Mean</i>	<i>13</i>	<i>16</i>	<i>20</i>	
MW-3D	0 – 1	16	---	---	Sand/Gravel
	0 – 3	10	7	11	Sand/Gravel
	<b>24 – 26</b>	7	9	10	Sand/Gravel
	26 – 28	9	13	15	Sand/Gravel
	28 – 30	5	11	15	Silt/Clay
	30 – 32	5	12	13	Silt/Clay
	<b>32 – 34</b>	11	24	33	Silt/Clay
	<b>38 – 40</b>	---	---	---	Silt/Clay

Boring	Sample Depth (ft.)	Arsenic (mg/kg)	Iron (mg/kg)	Mn <sup>a</sup> (mg/kg)	Stratigraphic Interval
	<i>Mean</i>	9	13	16	
MW-6D	0 – 1	11	---	---	Sand/Gravel
	0 – 3	13	9	15	Sand/Gravel
	<b>39 – 41</b>	17	27	46	Silt/Clay
	43 – 45	9	26	40	Silt/Clay
	47 – 49	7	25	35	Silt/Clay
	<b>53 – 55</b>	6	21	33	Silt/Clay
	<b>59 – 61</b>	8	32	68	Silt/Clay
	<b>DUP</b>	15	---	---	Silt/Clay
	61 – 63	8	27	37	Silt/Clay
	<i>Mean</i>	10	24	39	

<sup>a</sup> Manganese

The depths noted in bold typeface indicate samples selected for electron microprobe analysis.

Eleven of the above soil samples, highlighted in bold in Table 2, were submitted to the Electron Microprobe and Scanning Electron Microscope Facility of the Department of Geosciences of the University of Massachusetts at Amherst to identify the presence of arsenic-bearing minerals in the samples. The samples selected for microprobe analysis were from depths within the screened intervals of the corresponding monitoring wells. Arsenic was detected in 4 of 11 samples. Table 3 summarizes the chemical composition of each arsenic-bearing sample and associated mineralogy:

Table 3. Arsenic mineralogy and chemical composition

Boring	Sample Depth (ft.)	Composition
MW-1	8 – 10	Poorly crystalline, hydrous alteration products often associated with biotite; and iron-rich clinosafflorite [(Co,Fe,Ni)As <sub>2</sub> ]
MW-1	10 – 12	altered iron oxides
MW-3	24 – 26	iron-rich clinosafflorite [(Co,Fe,Ni)As <sub>2</sub> ]
MW-3	32 – 34	Arsenopyrite (FeAsS)

The mineralogy results confirmed the presence of arsenic-bearing minerals and weathering products in soil. Clinosaflorite was identified in samples from borings MW-1 (8 to 10 feet) and MW-3 (24 to 26 feet). Of the minerals identified, this cobalt-bearing mineral has the highest weight percent of arsenic (> 70%) (Jercinovic, 2004). This finding is similar to that reported by Hon et al. (2002), which indicated that the highest arsenic concentrations were detected in soil containing cobalt. The soil study conducted by Hon et al. found elevated concentrations of arsenic (20 to 800 mg/kg) in sections of overburden within a zone traversing north-south across central Massachusetts. Bedrock underlying these areas of elevated arsenic concentrations contained cobaltites (30 to 50% by weight arsenic) and pyrites.

It must be noted that there is no correlation in arsenic concentrations between the soil laboratory results and microprobe analysis. As concluded in the UMass report, “...it can be stated with certainty that arsenic occurs within solid phases within these four samples”, however, “... it cannot be concluded that arsenic does not occur in the others, only that mapping of the exposed cross section did not reveal any” (Jercinovic, 2004). This apparent discrepancy is related to the differing analytical methods between electron microprobe analysis and standard bulk laboratory analysis. Electron microprobe analysis analyzes the two-dimensional surface of a prepared sample rather than the entire digested bulk sample in traditional laboratory analysis.

In summary, subsurface samples of unconsolidated deposits at the site contained arsenic-bearing minerals and elevated concentrations of arsenic. Although bedrock was not sampled, descriptions of bedrock, as observed in subsurface samples from the site, are consistent with published regional data indicating elevated arsenic levels in rock. The second line of evidence required to demonstrate that arsenic is naturally occurring at the site was therefore established.

## **6. THIRD LINE OF EVIDENCE: GEOCHEMICAL CONDITIONS**

### **6.1 General Arsenic Geochemistry**

The fact that arsenic-bearing minerals are present in soil and bedrock does not by itself indicate that arsenic will be present in groundwater. The third and final line of evidence that observed concentrations of arsenic in groundwater are naturally occurring required a demonstration that the geochemical conditions in the aquifer were conducive to mobilization of arsenic. The dissolution of arsenic from soil and/or bedrock into groundwater is highly dependent on geochemical conditions in the aquifer. Most arsenic in groundwater occurs in one of two oxidation states, arsenate [As(V)] or arsenite [As(III)]. Arsenite is more mobile and is the predominant species under reducing conditions (low dissolved oxygen and oxidation-reduction potential (ORP)) and at pH < 9.0 (Blum and Renshaw, 2003).

Arsenic is strongly adsorbed by clay minerals and hydroxides of iron, aluminum and calcium, which coat clay particles. The soil adsorption capacity is influenced by pH and ORP, both of which affect the net charge of the hydroxide ion and the oxidation state of arsenic (Welch et al., 2000; Blum and Renshaw, 2003). When arsenic associated with iron oxides and sulfide minerals such as arsenopyrite dissolves under near-neutral pH conditions, iron forms an oxyhydroxide solid, and arsenic becomes a negatively charged ion. Under neutral and low pH conditions, iron particles have a positive charge and bind with arsenic, resulting in decreased concentrations of arsenic in groundwater. As the pH increases, iron hydroxide colloids become negatively charged and repel arsenic, resulting in its mobilization. The iron hydroxide particle remains insoluble and, unlike conditions in soil, there is less correlation between iron and arsenic concentrations in groundwater (Blum and Renshaw, 2003).

### **6.2 Site-Specific Geochemistry**

The arsenic mobilization model described above was evaluated as part of this study by measuring geochemical parameters pH, ORP, and dissolved oxygen each time groundwater was sampled for arsenic. Between October 2001 and August 2004, eight rounds of groundwater sampling were conducted on some or all of the ten monitoring wells. The final four rounds of sampling included the entire set of wells. Measured parameters included the above field parameters, as well as dissolved arsenic, iron, and manganese.

Groundwater from monitoring wells screened entirely in the upper sand/gravel unit did not contain arsenic above method detection limits (MDLs). Groundwater from wells screened across both the upper sand/gravel and the lower silt/clay units contained arsenic at concentrations ranging from below MDLs to 0.027 mg/l. Groundwater from wells screened in just the lower silt/clay unit contained the highest detected concentrations of arsenic, up to 0.082 mg/l. Except for well MW-5R, lower concentrations were detected in groundwater from the bedrock wells. Table 4 summarizes the average sampling results for each well. The values included in the table are the averages from four rounds of sampling: February 2003, November 2003, April 2004, and August 2004. The table is arranged in order of stratigraphic interval.

The highest average arsenic concentrations, ranging from 0.032 mg/l to 0.082 mg/l, were detected in groundwater from monitoring wells MW-2D, MW-6D, and MW-5R. The geochemical conditions measured in these wells were:

- pH between 7 and 8
- low dissolved oxygen (<1.2 mg/L)
- relatively low ORP (i.e., reducing conditions)

Table 4. Average groundwater concentrations and measurements: Feb. 2003 – Aug. 2004

Well ID	Screened Interval <sup>a</sup>	Sample Depth (ft.) <sup>b</sup>	PH (SU)	DO <sup>c</sup> (mg/l)	ORP <sup>d</sup> (mV)	Arsenic (mg/l)	Iron (mg/l)	Mn <sup>e</sup> (mg/l)
MW-3S	<b>Sand/</b>	14	5.0	8.0	218	<0.004	0.02	0.01
MW-4S	<b>Gravel</b>	14	4.7	7.3	313	<0.004	0.03	0.03
	<i>Mean</i>		<b>4.9</b>	<b>7.7</b>	<b>266</b>	<b>&lt;0.004</b>	<b>0.03</b>	<b>0.02</b>
MW-1S	<b>Sand/Gravel and Silt/Clay</b>	7–8	5.0	3.9	114	0.01	0.10	0.13
		12	5.8	0.6	157	0.02	---	---
		19	5.3	3.5	70	0.02	0.65	0.24
MW-2S		11–12	6.3	5.0	101	<0.004	<0.025	0.01
		19	6.1	5.0	121	<0.004	0.01	0.01
MW-3D		25	5.5	4.0	243	0.01	0.04	0.11
		30	5.7	5.7	261	<0.004	---	---
		34	5.7	3.0	216	0.02	0.12	0.17
	<i>Mean</i>		<b>5.7</b>	<b>3.8</b>	<b>160</b>	<b>0.001</b>	<b>0.16</b>	<b>0.11</b>
MW-2D	<b>Silt/Clay</b>	18	7.3	1.1	14	0.08	0.07	0.27
		24	7.2	0.3	57	0.07	---	---
		30	7.2	1.2	12	0.06	0.05	0.23
MW-6D		42	7.7	0.5	91	0.05	0.30	0.06
		52	7.4	0.1	-27	0.03	---	---
		62	7.6	0.5	29	0.05	0.34	0.07
	<i>Mean</i>		<b>7.4</b>	<b>0.6</b>	<b>29</b>	<b>0.06</b>	<b>0.19</b>	<b>0.16</b>
MW-3R	<b>Bedrock</b>	140-170	8.6	1.7	141	0.03	0.08	0.03
MW-5R		150-240	7.8	0.7	-30	0.08	0.31	0.15
MW-6R		165-180	8.9	1.0	21	0.03	0.03	0.02
	<i>Mean</i>		<b>8.4</b>	<b>1.1</b>	<b>44</b>	<b>0.05</b>	<b>0.14</b>	<b>0.07</b>

<sup>a</sup> The overburden stratigraphic unit(s) across which the well screen is placed. Bedrock wells are open-hole construction and are cased from the ground surface to the top of competent bedrock.

<sup>b</sup> Sample depth is the depth at which the groundwater sample was collected using low-flow sampling techniques.

<sup>c</sup> Dissolved oxygen

<sup>d</sup> Oxidation reduction potential

<sup>e</sup> Manganese

Groundwater from two bedrock wells, MW-3R and MW-6R, contained slightly lower arsenic concentrations (0.03 mg/l), but exhibited higher pH values (8.6 to 8.9). The slightly lower arsenic concentrations may be due to the change in oxidation state from arsenite to the less mobile arsenate, which occurs at pH above 9.0. Groundwater from one bedrock well, MW-5, with an average concentration of 0.08 mg/l, contained higher concentrations than groundwater from the other two bedrock wells. This is likely due to the lower pH than that observed at the other bedrock wells, as well as to lower dissolved oxygen and very low ORP values, conditions that are favorable for the mobilization of arsenic.

Lower arsenic concentrations were detected in groundwater from overburden wells MW-1S, MW-2S, MW-3S, MW-3D, and MW-4S. The pH measurements for groundwater from these wells were all below 6.3, and ranged down to a pH of 4.7. Dissolved oxygen and ORP were also higher than in other wells.

The geochemical characteristics observed in groundwater indicate that the geochemical environment in the sand/gravel, and sand/gravel and silt/clay units is acidic, oxygenated, and oxidizing, as opposed to the slightly basic, low dissolved oxygen, and more reducing conditions found deeper in the silt/clay unit. As a result, the geochemical environment found in the silt/clay unit is more favorable for the dissolution of arsenic from mineral grains into the groundwater.

Although there is no apparent correlation between arsenic concentrations in soil, aquifer lithology, and arsenic concentrations in groundwater, that lack of correlation can be explained by the heterogeneous nature of arsenic distribution in the unconsolidated deposits and the fact that groundwater samples are representative of a larger volume of aquifer than can be represented by a given soil sample collected from a similar depth. Particularly relevant to the overall evaluation of the data is the fact that the silt/clay unit contains more mineral surface area per unit of aquifer (more and smaller grains), thus exposing more mineral surface for possible dissolution of arsenic-bearing

minerals. Coupled with the lower rate of groundwater flow, which likely limits introduction of oxygen into the aquifer, it is not surprising that arsenic concentrations are higher in groundwater from the silt/clay unit than in the more permeable sand/gravel deposits.

Overall, the highest arsenic concentrations in groundwater at the site were detected in wells exhibiting a range of geochemical parameters consistent with those considered favorable for arsenic mobilization. Arsenic was also detected in some groundwater samples exhibiting one or more geochemical parameters outside the optimal range, which is to be expected in any data set and does not preclude the evidence supporting the presence of naturally occurring arsenic at the site. The favorable geochemical conditions in groundwater for the mobilization of arsenic therefore confirm the third and final line of evidence required to support the hypothesis that detected concentrations of arsenic in groundwater at the site are naturally occurring.

## 7. CONCLUSIONS<sup>1</sup>

The results of this study strongly indicated that arsenic detected in groundwater at the site can be attributed to naturally occurring geologic conditions and is not the result of anthropogenic activities. This conclusion is based on the following lines of evidence:

1. No anthropogenic sources of arsenic were identified, either historically or under current use conditions.
2. Arsenic was detected in bulk chemical analysis, and arsenic-bearing minerals are present in overburden materials that were derived from local bedrock. Local mapping of bedrock and the type of bedrock observed during drilling of bedrock wells at the site is consistent with rock types known to contain high concentrations of arsenic, and observations of bedrock samples from the on-site shaft and tunnel indicated the presence of small sulfide mineral grains.
3. The geochemical conditions favoring mobilization of arsenic from geologic materials into groundwater were reported in groundwater from wells installed in both overburden and bedrock at the site.

As a result of these findings, site closure under the MCP was achieved, and no further investigatory or remedial actions were necessary.

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<sup>1</sup> This article represents the opinions and (legal) conclusions of the author(s) and not necessarily those of the MWRA.



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